

EXPERIMENTAL INVESTIGATIONS OF THE HIGH-TEMPERATURE STABILITY OF SIDERITE: IMPLICATIONS FOR THE ORIGIN OF ALH 84001 CARBONATES.

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The carbonates in ALH 84001 have assumed an importance far beyond that initially assigned them, as simple indicators of aqueous or hydrothermal activity on Mars [1]. Their association with organics that may also be martian has led to the proposition that the carbonates themselves may be biologically deposited [2]. Counter proposals for the petrogenesis of these carbonates have concentrated on high temperature origins, either as immiscible carbonate/silicate liquids [3] or preexisting carbonates that have been molten and redistributed by shock [4]. We have conducted experiments at high temperature and pressure on a carbonate composition that is representative of many of the ALH carbonate analyses reported by Harvey and McSween [4], $\text{Ms}_{40}\text{Sd}_{40}\text{Cc}_{20}$ ($\text{Mg}:\text{Fe}:\text{Ca} = 2:2:1$). Our results, while preliminary, are consistent with existing phase diagrams [5] for siderite stability and argue against an anhydrous high temperature origin for the ALH 84001 carbonates.

Experimental: Reagent and analytical grade MgCO_3 and CaCO_3 were dried at 200-250°C and mixed with natural siderite in the proportions given above. In order to further approximate the natural assemblage, ~1 wt.% natural MnCO_3 was also added. The mixture was ground under acetone in an agate mortar and redried at 200°C. Aliquots of the starting composition were loaded into Ni capsules. These capsules were then loaded into a piston cylinder assembly using BaCO_3 as a pressure medium. Except for the capsule material, the dimensions and configuration of the assembly are the same as those for the immiscible carbonate-silicate liquid experiments of [5]. A series of reconnaissance experiments were run in a piston cylinder at 10 kbar and 500, 600, 800, 1000, and 1200°C. Run duration at temperature for our experiments was ~24 hours. Because of the capsule material, we anticipate that redox conditions were near that of Ni-NiO, approximately that inferred for the martian mantle [6]. We cannot guarantee that our charges were anhydrous, but we believe,

based on past experience, that any water present will react with the Ni capsule, with subsequent loss of H_2 from the charge. In the lowest temperature runs, 500-600°C, it is not clear that equilibrium was achieved.

The capsules were not welded, but relied instead on a mechanical seal. We believe this was sufficient to seal the capsule because: (i) 10 kbar exceeds the yield strength of Ni metal at room temperature and (ii) all runs above 500°C were annealed at pressure and 500°C for four hours. [The yield strength of Ni decreases with increasing temperature.] For runs above 500°C, the contact between the lid and the capsule became very hard to locate, evidence that the pressure fit was sufficient to seal the capsule. For comparison, a series of experiments run in graphite capsules clearly did not remain sealed and lost CO_2 .

Run products were evaluated using a JEOL SEM and various Cameca electron microprobes. On the JSC Cameca SX-100, a thin-window energy dispersive system allowed the detection of C x-rays to facilitate the identification of carbonates *versus* oxides.

Results: At 500° and 600°C calcite and magnesite have reacted to form dolomite and some grain coarsening appears to have occurred. Only minor Mg and Mn has entered the siderite. The reaction of calcite and magnesite appears to be facilitated by the fine grain size of the Ca and Mg components. At 600°C the presence of minor Fe-oxides indicates that there may be incipient decarbonation of siderite. At 800°C most of the siderite has decomposed. The entire capsule wall is rimmed by (Ni,Fe)O (ferroan bunsenite?), and the phase assemblage of the interior of the charge is dominated by (Fe,Ni)O, magnesite, and dolomite. By 1000°C there is no siderite present; the magnesite is also beginning to decompose; and Mg in the (Fe,Ni) oxide phase has increased. Magnesite and dolomite grains have coarsened. Some voids are present, indicating the presence of a fluid phase, presumably CO_2 . By 1200°C the charge has begun to melt. Ferroan bunsenite(?) coexists

with a solid Ca-rich carbonate and a quenched carbonate liquid that is richer in Mg and Fe than the solid. The 1200°C charge has large void pockets, and the Mg content of the oxide phase has increased.

Interpretation: In effect, our experiments have rediscovered the wheel. Earlier investigations of siderite stability have shown that at 5-10 kbar siderite decomposes to magnetite and graphite [7,8] at ~500-700°C. There is disagreement in detail over the exact temperature because of the difficulties in attaining equilibrium at these low temperatures, but the general chemographic topology of this region of the Fe-O-C system is well understood [e.g., 7]. The temperature of decomposition, in addition to being a function of pressure, is also a function of f_{O_2} [7]. At lower f_{O_2} 's the stability field of siderite is slightly enlarged. Our main contribution to this issue has been to add other components to the system (Ca and Mg). To first order, it appears that the presence of Ca and Mg have only a limited effect on siderite stability.

Implications for martian carbonates: To the extent that the carbonates of ALH 84001 are the products of near-equilibrium processes (something yet to be demonstrated), we feel it is difficult for them to have been produced by anhydrous igneous processes. As our experiments have shown, the siderite component of our carbonate assemblage decomposes at relatively low temperatures (600-800°C). And to some extent we have unintentionally torqued our experiments towards maximum siderite stability: (i) The pressure of our experiments is 10 kbar, which on Mars corresponds to a burial depth of ~100 km. This is approximately the maximum thickness thought possible for the martian crust. Consequently, at higher levels in the crust (i.e., at lower pressures), siderite will decompose at even lower temperatures. (ii) The f_{O_2} of our experiments approximates that of the martian mantle [6]. Because the uppermost surface of Mars is extremely oxidizing [9], we envision that crustal f_{O_2} 's will typically be intermediate between those of the mantle and those at the surface. And at higher f_{O_2} 's, siderite will decompose at lower temperatures. Thus, the net

effect of our experimental conditions should be to promote siderite stability as compared to conditions within the martian crust.

Consequently, we favor a low temperature origin for the ALH 84001 carbonates, probably in an aqueous environment. Temperatures above ~500°C do not favor the stability of carbonates with a significant siderite component. The refractory nature of pure carbonates indicates to us that, if the temperature of origin was low, the conditions were likely to be aqueous or hydrothermal.

This conclusion is ostensibly at odds with the phase diagram used by [4] and constructed by [10]. The reasons for this are somewhat unclear, but the phase diagram of [10] was largely determined by the one-hour experiments of [11], who worked at somewhat higher pressure (15 kbar) and who sometimes added $NaHCO_3$ to their experiments "to inhibit oxidation" of the siderite [11]. Therefore, the experimental conditions of the two sets of experiments are not necessarily comparable.

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